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(54) IMPROVEMENTS IN THERMAL RADIATION SENSORS

(71) We, SENSORS, INC., a corporation organised and existing under the laws of the State of Michigan, United States of America, of 303 West Ann Street, Ann Arbor, State of Michigan, 48109, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with radiation sensing structures and methods for their manufacture.

The invention is especially applicable to radiation sensing thermocouples or thermopiles, and their manufacture.

With such devices, the temperature rise caused by radiation is sensed by a junction (thermocouple detector) or a series of junctions (thermopile detector). Practical advantages of this type of sensor include room temperature operation, some responsiveness to differing wave lengths of radiation, and a direct signal voltage without need for a bias voltage supply. However, some distinct disadvantages of some past thermocouples which have limited their usage are: fragile structure, slow speed of response to changing radiation, and lack of uniform response to differing wave lengths of radiation.

Examples of prior art structures are shown in the U.S.A. patents Nos. 3,483,045 and 3,405,272. Typically a thin plastics film material is adhesively attached to a backing metal and bridges a recess therein. Or, a thin supporting film of aluminium oxide is affixed around an opening in an aluminium heat sink by epoxides or adhesive resins. While such structures can be satisfactory for certain uses, assembly costs and the difficult manufacturing procedures are obvious disadvantages. Also suitable uses for such structures are limited because of their fragile structure. Less obvious perhaps are of disadvantages related to both manufacture and use which stem from the adhesives. The adhesives are likely to decompose in manufacture or use and contaminate the coating process or the sensing operation.

One aspect of the present invention resides in a method for making a film-type thermal sensing structure in which a preshaped blank is treated on at least one surface to form from material of the blank a chemical composition in the form of a high strength electrically insulative coating and blank-material backing is removed from the coating over a prescribed area to leave an exposed, thin film supported about its entire periphery by and unitary with the remaining blank material and spanning a recess in the blank, and in which thermoelectric sensing material is deposited on the peripherally supported film.

Another aspect of the invention is a method for manufacturing a thermal sensing structure in which an aluminium metal blank is shaped to have a cavity therein and the metal blank is anodized to form an anodized layer of predetermined thickness and in which the anodized layer is exposed on opposed interior and exterior surfaces of the cavity to form a film supported by and unitary with the remainder of the metal blank about its entire periphery, and thermoelectric materials are deposited on the film in a predetermined manner with overlapping portions of the thermoelectric materials forming thermocouple junctions and some of said junctions overlying the metal of the blank.

The invention includes a thermal radiation sensing structure comprising a thin film peripherally supported on a backing member, such film comprising a chemical reaction product formed from the backing member unitary with the backing member, and a radiation sensitive thermo-electric material supported by the thin unitary film.

Thus the peripherally supported film can be adhesive free and of very low mass, low heat capacity and low heat conductivity. Also, use of high thermoelectric power semiconductor materials is made practicable because it is possible for a thin film to be subjected to various treatments, including heat treatments during deposition of the materials, without degradation of the film in any way.

In preferred embodiments amorphous aluminium oxide (Al_2O_3) is produced in a hard coat electrolytic anodizing process working with substantially pure aluminium. Other backing materials and films are within the scope of the invention. For example, aluminium alloys, tantalum, silicon and other materials having suitable heat and electrical conduction properties and which form coating layers of suitable properties such as high strength, low heat conductivity, and electrically insulating. Such coating layers will generally be formed by oxidation, however, suitable coating layers can be formed by other chemical reactions.

The thickness of an anodized layer can be controlled by the voltage supplied during anodizing. Unlike the usual anodized coatings on aluminium for protection or decorative purposes, a barrier-type oxide coating is utilized in the preferred embodiments. This type of coating is formed in an electrolyte with little or no capacity to dissolve the oxide layer. The result is non-porous (pinhole-free), dense, and hard surface layer.

Several processes are possible for removal of backing after anodizing so that a thin hard film bridging a recess in the metal backing is exposed without possibility of damage to the film. This film is unitary, that is, one with the metal around its entire periphery, rather than being made integral by adhesives as in the prior art. Because the aluminium oxide is an amorphous form, not crystalline, the thermal conductivity is low. With this film, a hot thermocouple junction e.g., is more likely to lose absorbed heat by radiation.

Thermoelectric materials can be vapour-deposited onto the thin unitary film. Semiconducting materials of high molecular weight having the advantages of high thermoelectric power, low thermal conductivity, and high electrical conductivity are preferred. Examples are bismuth telluride, lead telluride and lead selenide. While these materials have good inherent electrical characteristics, vapour deposited films of these materials have not been successfully applied in the past in film-type sensors. Weaknesses in the physical characteristics of the prior art structures placed limitations on the vapour deposition process. Because of this it is felt that degradation of electrical properties of the semiconductor materials resulted and excessive electrical noise, low thermoelectric power, and high electrical resistance were experienced. Such faults are believed to be traceable to imperfect crystallinity of the thermoelectric coatings and to barrier layers between crystalline boundaries.

One specific disadvantage of the thin film substrates of the prior art is that they cannot be heated sufficiently, especially in a vacuum. The substrate materials or the adhesives, or both, were not sufficiently temperature stable; e.g. melting occurred or they decomposed with an evolution of gas spoiling any vacuum process. Contrary to that experience, unitary films, such as the aluminium oxide film, possible with the present invention, are extremely stable and can be heated to the proper temperature for deposition of semi-conductor layers of high quality without damage to the substrate or without degradation of the vacuum. Also, enhanced thermoelectric properties result. Further, the dynamic range for a sensor of the present invention is considerably increased over the prior art structure. Because of high temperature stability it can be used to measure high power sources, such as CO_2 lasers.

The films formed in the course of the method of the present invention need not be flat. To improve the absorption of radiation the sensor may be shaped in the form of a black body cavity, e.g. conical. The advantage of the cone (and similar cavity shapes) is that the cone will absorb radiation of all wavelengths almost perfectly, even if coated on the inside with an imperfectly absorbent material. Therefore a thermopile made with a conical collector would be almost truly standard detector whose electrical output would depend substantially only on the radiant power entering the cone (or similar cavity) and not on spectral distribution of the incident radiation. This property becomes more significant with longer wavelengths (beyond ten micrometers) where the absorption by black, substantially flat, layers begins to decrease.

The invention is further described, by way of example, with reference to the accompanying drawings, in which:—

Figs. 1, 2 and 3 are schematic cross-sectional views of a metal blank being processed in the method of the present invention,

Fig. 4 is a top plan view of a thermal sensing structure in accordance with the invention,

Fig. 5 is a schematic cross-sectional view of the sensing structure,

Fig. 6 is a schematic cross-sectional view

of a conical embodiment of the invention,

Fig. 7 is a schematic cross-sectional view of vacuum coating apparatus for carrying out the method of the invention,

Fig. 8 is a schematic view of a portion of a thermal sensing structure showing a thermocouple junction structure,

Fig. 9 is a schematic plan view of a thermal sensing structure in accordance with the invention,

Fig. 10 is a schematic cross-sectional view of a thermal sensing structure in accordance with the invention, and

Fig. 11 is a cross-sectional view of a specific embodiment of the invention.

In carrying out the preferred embodiment of the invention, a suitable metal such as aluminium is shaped by punching, drawing, machining cutting, and/or forging. In the specific embodiment of Fig. 1, a cavity 20 is formed in a metal blank 21. Its exterior surface 24 is polished to a high degree, e.g. by mechanical polishing and/or electrolytic-polishing. The object is to produce an extremely smooth surface avoiding pores or a reentrant type surface.

After shaping as desired and polishing of the surface 24, the polished surface is anodized to form a thin, hard, barrier-type anodized layer 26.

In a typical thermopile application, the overall thickness of the metal blank measured along a side wall 28 would be between about 1/16th and 1/8th inch. The metal blanks can be fabricated from sheet stock aluminium with recessed portions formed, e.g. before anodizing. The blanks are generally cut from the sheet stock before anodizing but can be cut after anodizing, depending on the cutting apparatus, if mechanical damage to the surface can be avoided. Suitable thicknesses for the anodized layer 26 are from one tenth of a micron up to about one micron.

A desirable type of anodized layer can be made in dilute solutions of ammonium citrate plus citric acid or ammonium tartrate plus tartaric acid at a pH of about five. A typical electrolyte includes distilled water and 0.5 grams per litre of ammonium citrate plus 0.5 grams per litre of citric acid. The object is to avoid establishing porosity in the oxide layer due to erosion by the electrolyte solution.

The thickness of the layer formed on the aluminium is determined by the anodizing potential used, with approximately 13.5 angstrom units of thickness being developed with one volt of anodizing potential. It should be noted that a chemically formed unitary support layer can be made in ways other than electrolytic anodizing and can be made from metals other than aluminium.

The coating can be carried out by anodizing the entire blank 21 or only the surface 24. When the entire blank is anodized, the anodized layer at the bottom surface of the recess or a portion thereof must be removed. This can be done by abrading such surface or, with a hydroxide etchant such as concentrated potassium hydroxide.

As shown in Fig. 3, with the metal surface of the recess 20 exposed, an etchant 30 which is not harmful to the coating layer 26, is used to remove the backing metal 32. A typical example of such an etchant is 25% hydrochloric acid solution. What remains, an oxide film, is unitary with the metal blank. As is more evident from Fig. 4, this film is supported around its entire periphery 34. Alternatively the exposed backing metal can be removed by a process such as photo-etching, chemical milling, or photochemical milling. Such processes may also be used for selective area removal of the anodized layer.

Referring to Fig. 5, because of the extreme thinness and high strength of the film which can be formed, a thermocouple can be manufactured with a film which is more likely to lose heat by radiation. At the same time the unitary film maximizes the heat contact along the direction indicated by the arrow 38 because of its intimate contact and because the need for the thermally insulating adhesive layer of the prior art is not present. Also, because of the good electrical insulation properties of the oxide film, effective electrical insulation is provided to prevent a short circuit at the heat sink 22 formed by the remaining annular part of the blank 21 with the layer 26 thereon.

In forming a thermocouple junction, a layer 40 of thermoelectric material extends from the peripherally supported film onto the heat sink 22 and, a layer 42 of a differing thermoelectric material, extends from the film supported laytr 44 towards another portion of the heat sink 22. A hot junction 46 is formed on the thin film. Leads 47 and 48 connect the thermoelectric materials to a measuring instrument such as a suitably sensitive galvanometer (not shown). Lead attachment metals, such as silver, gold or indium, are vapour deposited on the thermoelectric material at the lead contact areas 49, 50. Leads are attached by soldering, conductive metal cement, or similar semi-conductor device manufacturing methods. Fine metal wires, e.g. gold, are used for leads 47 and 48.

Configurations other than planar are made possible by the present invention. Such non-planar shaping of the oxide layer e.g. cavity configurations can be widely diversified. Non-planar configurations bring about the ability to manufacture one of the most efficient types of radiation absorbers,

a conical cavity as shown in Fig. 6. The interior surface 60 can be coated with material, such as lamp black, platinum black, or gold black to enhance absorption. This provides the characteristic "black body cavity" absorption especially suitable for accurate sensing of radiation containing varying wave lengths and in effect provides substantially a perfect absorber.

Referring to Fig. 6, a conically shaped oxidized layer 62 supports thermoelectric materials forming, for example a hot junction 64. A cold junction 66 is supported on a heat sink 68 as shown in Fig. 6.

The dimensional characteristics, that is, thickness of the conical oxide layer formed and the heat sink shown in Fig. 6, can be as described earlier in relation to Fig. 5. A plurality of hot and cold junctions positioned around the cone can be connected for forming a thermopile.

Suitable thermoelectric materials include bismuth and antimony which have been used in the prior art. And, among the other semiconductor materials suitable for use with the present invention as thermoelectric materials are lead telluride, and the like. The semi-conductor materials are preferred because of their higher thermoelectric power and lower thermal conductivity. With the unitary, highstrength sensing structure of the present invention, which does not rely on an adhesive for holding a film to the metal backing, deposition of semi-conductor materials can be carried out at high temperatures with both the film and metal blank being heated.

Referring to Fig. 7, apparatus is shown for carrying out a vapour deposition operation. A chamber 70 within a bell 72, is evacuated. A furnace 74 includes two boats, such as 76, for holding thermoelectric materials. The furnace is heated by resistance heating, electron bombardment, or the like. The object to be coated is located at 78 and a heater 80 maintains it at desired temperature. A shutter 82 is located between the source of metal and the object to be coated to control flow of metal. A mask 84 is provided in close juxtaposition to the object to be coated. The mask 84 controls the configuration of the applied coating.

Where a plurality of coatings is to be applied, a mask will be used in a selective position while one of the materials to be coated is heated in its receptacle. After the desired thickness coating of that material is applied, the mask is shifted and a second material is heated and vapour deposition of desired weight and configuration takes place. A plurality of masks may also be used. Also under certain circumstances photo-etching could be used to obtain selective surface coating.

Fig. 8 shows an enlarged partial view of the result of the masking and vapour deposition operation. A first thermoelectric material 85 is applied and extends between a basically metallic heat sink 86 and a thin peripherally supported film 88; a dividing line 89 indicates the separation between the heat sink and the peripherally supported film. In the masking operation a second thermoelectric material 90 is applied overlapping the first material, as shown to form a hot junction 92 on the film. A cold junction 94 is formed on the heat sink where the two materials overlap etc..

Multiple aperture masks are used so that multiple junction thermocouples can be made in a two coating step operation. Figure 9 shows the results of such thermopile fabrication. In the specific embodiment illustrated, twenty junctions are formed over 2.0 by 0.2 mm. areas $a \times b$. The junctions are connected in series and through leads 96 and 95 to a suitable meter (not shown). The hot junctions 98 on the thin film are covered with a suitable radiation absorbent material, such as lamp black layer, shown by dash-line 99. The peripheral edge of the thin film is shown diagrammatically by solid line 100.

Fig. 10 shows a typical thermoelectric circuit in which a detector element 102 is housed within a chamber 104 with a radiation transmitting window 106. The leads 107 and 108 are typically connected to a meter or amplifier means 109. The chamber 104 can be evacuated or can be filled with an inert gas, such as argon. The structure can be fabricated to a standard dimension package, e.g. a JEDEC TO-5 transistor package.

The sensing structure in accordance with the present invention can be supported on a suitable probe with or without a protective chamber and evacuation. Suitable materials for a protective window for non-evacuated chamber protection of the structure include potassium bromide, polyethylene film or a zinc sulphide crystal or compact.

Details of a specific embodiment in which a sensing device is mounted in a standard intermediate size transistor package (TO-5) are shown in Fig. 11. A thin film radiation sensing structure 112 (with absorbent coating) is mounted on a support structure 114 within a case 116. Fine highly-conductive wires 118, 120 connect the sensing materials to signal leads 122, 124, at solder joints 126, 128, respectively. The signal leads 122, 124, where they pass through a case closure 130 are surrounded by glass insulated seals 132, 134. A case earth lead 136 is electrically connected to the case closure 130. The support structure 114 is joined to the case cover 130 by thermally conductive cement

137.

A radiation transmitting window 138 is joined to the case 116 by suitable cement 140. The overall dimension can be made to conform to substantially any standardized transistor part, or the like. Control of the enclosure atmosphere e.g. vacuum or inert gas, can be readily provided.

In addition to electrolytic anodizing of aluminium and aluminium alloys to form a coating layer, a unitary film for supporting sensing material can be formed by other methods and can be other than oxide coating layers. For example, plasma anodizing can be used to form Al_2O_3 and AlN films on aluminium and to form Ta_2O_3 on tantalum. A SiO_2 layer can be thermally oxidized on silicon; also a silicon nitride layer (Si_3N_4) can be formed by chemical reaction at the surface of the silicon blank. Silicon under certain circumstances can have advantages because of its thermal conductivity and semi - conductor electrical properties.

Advantages of the hereinbefore described embodiments of the invention include: greater ruggedness because of both the inherent strength of the film and because the film is unitary with the blank, greater ease of manufacture and consequent lower production costs, the capability of producing thin film support in a wide variety of configurations the capability of satisfactorily depositing semi-conductor materials having better thermoelectrical characteristics, and the production of wider range sensors of great temperature stability than previously available.

WHAT WE CLAIM IS:—

1. A method for making a film-type thermal sensing structure in which a preshaped blank is treated on at least one surface to form from material of the blank a chemical composition in the form of a high strength, electrically insulative coating and blank-material backing is removed from the coating over a prescribed area to leave an exposed, thin film supported about its entire periphery by and unitary with the remaining blank material and spanning a recess in the blank, and in which thermo-electric sensing material is deposited on the peripherally supported film.

2. A method as claimed in claim 1 in which said chemical composcition comprises an oxide layer.

3. A method as claimed in claim 2 in which the blank is of aluminium or aluminium alloys and in which said surface treatment of the blank comprises anodizing to form an anodized layer on the blank.

4. A method as claimed in claim 3 in which the anodizing is carried out in a weak acid solution substantially non-harmful to the anodized layer to form a hard, substantially pore-free anodized layer.

5. A method as claimed in claim 3 or 4 in which the anodized coating is between one tenth of a micron and one micron in thickness inclusive.

5. A method as claimed in claim 3 or 4 in which the anodized coating is between one tenth of a micron and one micron in thickness inclusive.

6. A method as claimed in claim 3, 4 or 5 in which the entire metal blank is anodized and the anodized layer on said prescribed area of the metal blank is exposed by removing at least a portion of the anodized layer from the blank in the region of said backing prior to the removal of the remaining backing from the coating.

7. A method as claimed in any of claims 1 to 6 in which the blank material backing is removed from the coating by etching, photoetching, chemical milling, or photochemical milling.

8. A method as claimed in any of claims 1 to 7 in which the metal blank is polished at the surface to be treated prior to treatment to form a substantially pitfree surface.

9. A method as claimed in claim 8 in which the polishing step includes electrolytic polishing.

10. A method as claimed in any of claims 1 to 9, in which the metallic blank is pre-shaped into a predetermined configuration presenting a recessed area prior to treatment, the blank-material backing being subsequently removed at said recessed area.

11. A method as claimed in claim 10 in which the recessed area has a cavity configuration.

12. A method as claimed in claim 11 in which the cavity has a conical configuration.

13. A method as claimed in claim 12 in which the interior surface of the conical cavity is covered with a radiation absorbent material, such as lamp black, after removal of backing from the internal surface of the cavity.

14. A method as claimed in any of claims 1 to 13 in which the peripherally-supported film is heated prior to depositing the sensing thermal-electric material.

15. A method as claimed in claim 14 in which the sensing material is deposited by vapour deposition.

16. A method as claimed in claims I to 15 in which a plurality of sensing materials is deposited on the peripherally supported film to form a thermoelectrical junction.

17. A method as claimed in claim 15 in which semi-conductor thermoelectric

materials are deposited in separate layers to form a thermocouple junction.

18. A method as claimed in claim 16 or 17 in which the separate layers of semi-conductor thermoelectric materials are deposited in partially overlapping relationship to form a plurality of hot junctions on the peripherally supported film and a plurality of cold junctions over the metal blank, the hot junctions and cold junctions being interconnected to form a thermopile.

19. A method as claimed in claim 18 in which the hot junctions are coated with a thermal radiation absorbent material.

20. A method for manufacturing a thermal sensing structure in which an aluminium metal blank is shaped to have a cavity therein and the metal blank is anodized to form an anodized layer of predetermined thickness, and in which the anodized layer is exposed on opposed interior and exterior surfaces of the cavity to form a film supported by and unitary with the remainder of the metal blank about its entire periphery, and thermoelectric materials are deposited on the film in a predetermined manner with overlapping portions of the thermoelectric materials forming thermocouple junctions and some of said junctions overlyng the metal of the blank.

21. A method as claimed in any of claims 1 to 20 in which the sensing structure is enclosed in a chamber containing a predetermined atmosphere.

22. A thermal radiation sensing structure comprising a thin film peripherally supported on a backing member, such film comprising a chemical reaction product formed from the backing member unitary with the backing member, and a radiation sensitive thermo-electric material supported by the thin unitary film.

23. A radiation sensing structure as claimed in claim 22 in which the film is electrically-insulative and the backing member is electrically conductive.

24. A radiation sensing structure as claimed in claim 22 or 23 in which the radiation sensitive material comprises at least one thermocouple and the backing member forms a heat sink for the thermocouple.

25. A radiation sensing structure as claimed in claim 24 in which the radiation sensitive material comprises a plurality of layers of thermoelectric material.

26. A radiation sensing structure as claimed in claim 25 in which a plurality of hot thermocouple junctions are supported on the peripherally supported film and a plurality of cold thermocouple junctions are supported over the heat sink.

27. A radiation sensing structure as claimed in claim 26 in which the hot and cold thermocouple junctions are interconnected through a measuring means.

28. A radiation sensing structure as claimed in claim 26 or 27 in which the hot thermocouple junctions are covered with radiation absorbent material.

29. A radiation sensing structure as claimed in any of claims 22 to 28 in which the peripherally supported film has a conical configuration.

30. A radiation sensing structure as claimed in claim 29 in which the interior surface of the conical configuration film is coated with a radiation absorbent material.

31. A radiation sensing structure as claimed in any of claims 22 to 30 in which the backing member comprises aluminium.

32. A radiation sensing structure as claimed in any of claims 22 to 31 in which the peripherally supported film comprises an oxide of the backing member.

33. A radiation sensing structure as claimed in claim 31 in which the peripherally supported film comprises an anodized layer of the aluminium backing member.

34. A radiation sensing structure as claimed in any of claims 22 to 33 in which the radiation sensitive material comprises semi-conductor material such as lead telluride, bismuth telluride or lead selenide.

35. A radiation sensing structure as claimed in any of claims 22 to 34 which is disposed in a chamber of predetermined atmospheric character encapsulating such structure the chamber including a window for passage of radiation to the radiation sensitive material, means being provided for connecting electrical leads to the radiation sensing material within such chamber.

36. A thermal radiation sensing structure when made by the method claimed in any of claims 1 to 21.

37. Methods of making thermal radiation sensing structures substantially as herein described with reference to the accompanying drawings.

38. A thermal radiation sensing structure substantially as herein described with reference to and as illustrated in Figs. 4 and 5 of the accompanying drawings.

39. A thermal radiation sensing structure substantially as herein described with reference to and as illustrated in Fig. 6 of the accompanying drawings.

40. A thermal radiation sensing structure substantially as herein described with reference to and as illustrated in Fig. 8 of the accompanying drawings.

41. A thermal radiation sensing structure substantially as herein described with reference to and as illustrated in Fig. 9 of the accompanying drawings.

42. A thermal radiation sensing structure substantially as herein described with reference to and as illustrated in Fig. 10 of the accompanying drawings.

43. A thermal radiation sensing structure substantially as herein described with reference to and as illustrated in Fig. 11 of the accompanying drawings.

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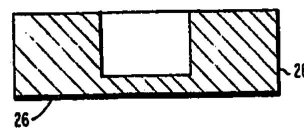
1381001 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG 2



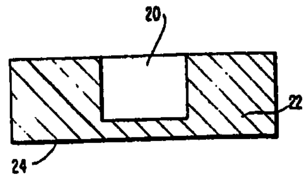


FIG. 1

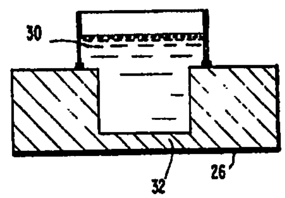


FIG. 3

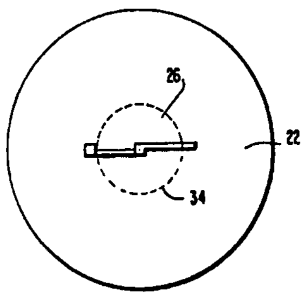


FIG. 4

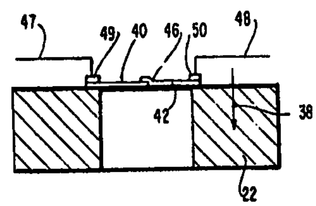


FIG. 5

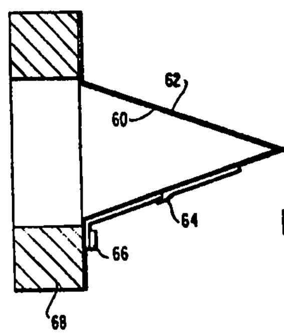


FIG. 6

1381001 COMPLETE SPECIFICATION

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Sheet 2

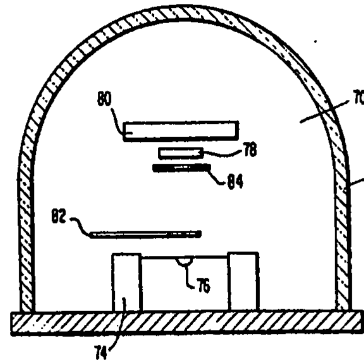

FIG. 7

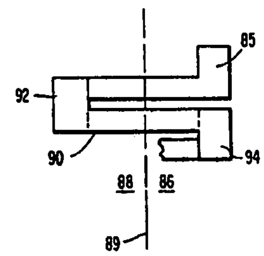

FIG. 8

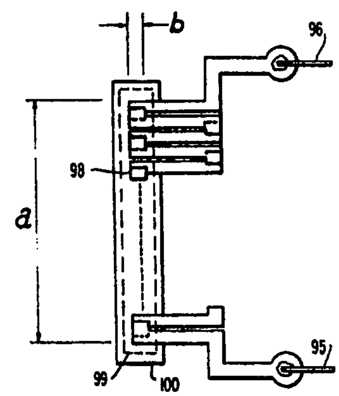

FIG. 9

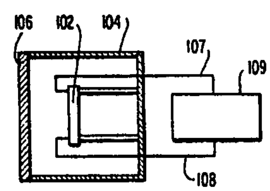

FIG. 10

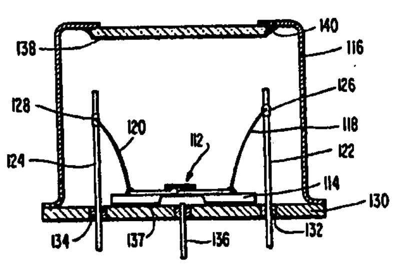

FIG. 11